Electronic Supporting Information (ESI)

for

Trap engineering in solution processed PbSe quantum dots for high-speed mid-IR photodetectors

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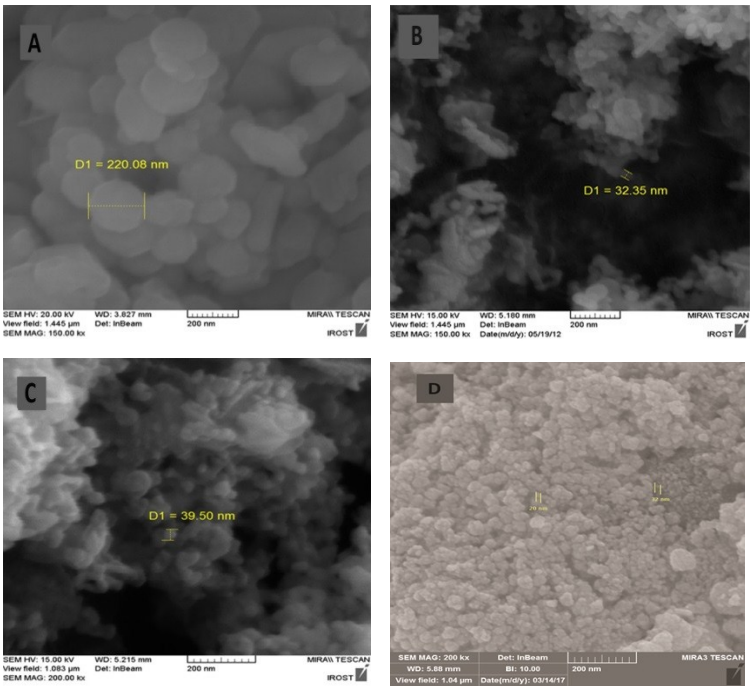

Fig. S1 | SEM images of the synthesised PbSe nanomaterials passivated with A) OAc^- (synthesised from $Pb(OAc)_2$), **B)** OAc^- (from $PbCl_2$), **C)** Cl^- (from $PbCl_2$), and **D)** I^- (from PbI_2)

Table S1 | **Chemicals and suppliers**

chemical	supplier	product number
lead chloride	Sigma-Aldrich	268690
lead acetate	Sigma-Aldrich	316512
lead iodide	Sigma-Aldrich	1088020250
sodium chloride	Sigma-Aldrich	S7653
potassium iodide	Merck	1096341000
sodium acetate	Merck	8187120100
2-propanol	Sigma-Aldrich	278475
ethanol	Merck	818760
acetone	Sigma-Aldrich	650501
oleylamine	Sigma-Aldrich	07805
selenium	Merck	1077140050
triphenylphosphine	Sigma-Aldrich	93092
n-hexane	Merck	104373
trioctyl phosphine oxide	Sigma-Aldrich	223301

Table S2| CASTEP calculation for PbSe/OAc: results I - energies

---------- ← SCF

SCF loop Energy Fermi Energy gain Timer ← SCF

energy per atom (sec) ← SCF

---------- ← SCF

Initial -7.49671264E+004 0.00000000E+000 6.86 ← SCF

```
   1 -7.01315084E+004  2.32286333E+000 -1.46533881E+002    190.80 ← SCF
   2 -7.28655997E+004 -3.22800390E-001  8.28512518E+001    334.98 ← SCF
   3 -7.30656642E+004 -7.09733128E-001  6.06255979E+000    460.41 ← SCF
   4 -7.30720275E+004 -7.67202256E-001  1.92828570E-001    590.81 ← SCF
   5 -7.30451982E+004 -1.10530059E-001 -8.13009875E-001    722.77 ← SCF
   6 -7.30443644E+004 -1.63002107E-001 -2.52654798E-002    881.62 ← SCF
   7 -7.30441763E+004 -8.23971386E-002 -5.69970198E-003   1023.62 ← SCF
   8 -7.30441114E+004 -8.89273009E-002 -1.96730153E-003   1181.46 ← SCF
   9 -7.30440970E+004 -5.54328496E-002 -4.34929918E-004   1319.43 ← SCF
  10 -7.30441043E+004 -3.37455866E-002  2.20634269E-004   1454.43 ← SCF
  11 -7.30441234E+004 -8.96759524E-003  5.76630265E-004   1583.32 ← SCF
  12 -7.30441363E+004  2.07358412E-003  3.92130564E-004   1704.62 ← SCF
  13 -7.30441469E+004  8.28877760E-003  3.21617240E-004   1814.81 ← SCF
  14 -7.30441523E+004  8.14802069E-003  1.62482503E-004   1929.90 ← SCF
  15 -7.30441537E+004  9.05236957E-003  4.45388670E-005   2036.37 ← SCF
  16 -7.30441545E+004  8.94840435E-003  2.44625890E-005   2135.97 ← SCF
  17 -7.30441550E+004  8.35118643E-003  1.29311914E-005   2233.12 ← SCF
  18 -7.30441550E+004  8.53558667E-003  1.54489264E-006   2326.36 ← SCF
  19 -7.30441550E+004  8.79263015E-003  4.85796477E-007   2410.43 ← SCF
  20 -7.30441550E+004  8.94617675E-003  1.65960808E-007   2495.78 ←SCF
--------------------------------------------------------------------------- ← SCF
Final energy, E           =  -73044.09847438     eV
Final free energy (E-TS)    =  -73044.15504538     eV
(energies not corrected for finite basis set)
NB est. 0K energy (E-0.5TS)      =  -73044.12675988     eV
Writing analysis data to AMS_DATA2.castep_bin
Writing model to AMS_DATA2.check

********************** Forces **********************
*          Cartesian components (eV/A)           *
* ------------------------------------------------ *
*              x         y         z     *
*                                        *
* H       1    7.93508   -26.55427   -45.69716 *
* H       2   -3.35016    -0.09383    -5.39010 *
* H       3   -7.92208    11.71600    -2.08103 *
* C       1   58.63601   -18.46350    -0.97633 *
* C       2  -55.70093    -6.76579   -39.45051 *
* O       1   98.64472  -419.00887    -7.05161 *
* O       2    7.76661    -9.30083     7.83123 *
* Se      1    0.13061     1.43740     0.42443 *
* Se      2   -0.77187     0.71434     0.36246 *
* Se      3   -1.55126    -0.26509     0.19929 *
* Se      4   -0.42569     0.27223    -0.21937 *
* Se      5   65.57869    24.91118    96.26970 *
* Se      6   -0.16422    -0.36298     1.02176 *
* Se      7   -0.83436     0.03551    -0.00852 *
* Se      8    0.10172    -0.11248     0.31740 *
* Se      9   -0.08959    -0.62864     0.33175 *
* Se     10   -1.43214    -0.39041    -0.15655 *
* Se     11    0.11478     0.20029     0.05839 *
* Se     12    0.53930     0.09287     0.01159 *
* Se     13   -0.19872    -0.04203     0.27515 *
```

```
* Pb      1     0.59705     0.34959     0.57851 *
* Pb      2     0.64016    -1.69878     0.91573 *
* Pb      3     1.76659    -0.61605     0.86549 *
* Pb      4    -0.28114    -0.44786     0.55551 *
* Pb      5  -174.71580   443.92602     1.06120 *
* Pb      6     2.42146     0.89188    -6.50159 *
* Pb      7     1.48318     0.35342    -0.84771 *
* Pb      8     0.37204     0.28433    -0.47692 *
* Pb      9     0.30082     0.38080    -0.74591 *
* Pb     10    -0.05873     0.10758     0.00486 *
* Pb     11     1.52897    -0.62633    -0.87004 *
* Pb     12    -0.26156     0.18601    -0.57927 *
* Pb     13    -0.79956    -0.48170    -0.03183 *
 ***************************************************
Pseudo atomic calculation performed for H 1s1
Converged in 13 iterations to a total energy of -12.4770 eV
Pseudo atomic calculation performed for C 2s2 2p2
Converged in 17 iterations to a total energy of -145.7151 eV
Pseudo atomic calculation performed for O 2s2 2p4
Converged in 22 iterations to a total energy of -423.8698 eV
Pseudo atomic calculation performed for Se 4s2 4p4
Converged in 17 iterations to a total energy of -253.2878 eV
Pseudo atomic calculation performed for Pb 5s2 5p6 5d10 6s2 6p2
Converged in 28 iterations to a total energy of -5275.7922 eV
Charge spilling parameter for spin component 1 = 0.41%
```

Table S3| CASTEP calculation for PbSe/OAc: results II – Mulliken and Hirshfeld analysis

Atomic Populations (Mulliken)

Species	Ion	s	p	d	f	Total	Charge (e)
H	1	1.03	0.00	0.00	0.00	1.03	-0.03
H	2	0.82	0.00	0.00	0.00	0.82	0.18
H	3	0.75	0.00	0.00	0.00	0.75	0.25
C	1	0.64	2.92	0.00	0.00	3.56	0.44
C	2	1.29	4.01	0.00	0.00	5.30	-1.30
O	1	1.72	5.06	0.00	0.00	6.78	-0.78
O	2	1.78	4.81	0.00	0.00	6.59	-0.59
Se	1	2.00	4.53	0.00	0.00	6.53	-0.53
Se	2	2.00	4.58	0.00	0.00	6.57	-0.57
Se	3	2.00	4.55	0.00	0.00	6.55	-0.55
Se	4	1.87	4.58	0.00	0.00	6.45	-0.45
Se	5	1.42	3.62	0.00	0.00	5.05	0.95
Se	6	1.85	4.63	0.00	0.00	6.48	-0.48
Se	7	1.95	4.60	0.00	0.00	6.55	-0.55
Se	8	1.90	4.60	0.00	0.00	6.50	-0.50
Se	9	1.93	4.54	0.00	0.00	6.47	-0.47
Se	10	2.00	4.57	0.00	0.00	6.57	-0.57
Se	11	1.87	4.57	0.00	0.00	6.44	-0.44
Se	12	1.93	4.58	0.00	0.00	6.51	-0.51
Se	13	1.87	4.57	0.00	0.00	6.44	-0.44

Pb	1	3.94	7.53	10.00	0.00	21.47	0.53
Pb	2	3.94	7.59	10.00	0.00	21.53	0.47
Pb	3	3.93	7.61	10.00	0.00	21.55	0.45
Pb	4	3.94	7.53	10.00	0.00	21.47	0.53
Pb	5	3.62	7.84	9.36	0.00	20.82	1.18
Pb	6	3.94	7.59	10.00	0.00	21.53	0.47
Pb	7	3.93	7.62	10.00	0.00	21.54	0.46
Pb	8	3.95	7.53	10.00	0.00	21.49	0.51
Pb	9	3.91	7.86	10.00	0.00	21.77	0.23
Pb	10	3.87	7.54	10.00	0.00	21.41	0.59
Pb	11	3.95	7.60	10.00	0.00	21.55	0.45
Pb	12	3.91	7.55	10.00	0.00	21.46	0.54
Pb	13	3.95	7.52	10.00	0.00	21.47	0.53

Bond	Population	Length (A)
H 1 -- Se 5	0.01	2.12587
C 1 -- O 1	0.02	0.95000
O 1 -- Pb 5	0.70	2.00217
H 3 -- C 2	0.42	0.95000
H 2 -- C 2	1.03	0.95000
H 1 -- C 2	0.09	0.95000
C 1 -- O 2	0.98	1.14000
C 2 -- Se 5	1.26	1.23566
H 3 -- Se 5	0.16	1.31933
C 1 -- C 2	0.46	1.54000
H 2 -- H 3	0.12	1.55135
H 1 -- H 3	0.12	1.55135
H 1 -- H 2	0.14	1.55135
C 1 -- Pb 5	0.94	1.59232
O 1 -- O 2	0.38	1.80441
H 2 -- Pb 6	0.03	1.81196
C 1 -- Se 5	0.92	2.05217
H 2 -- C 1	0.26	2.06142
H 1 -- C 1	0.25	2.06142
H 3 -- C 1	0.33	2.06142
H 2 -- Se 5	0.14	2.12356
C 2 -- O 1	0.30	2.16888
H 2 -- Se 6	0.13	2.25293
H 1 -- Pb 6	0.38	2.26814
C 2 -- Pb 5	0.71	2.30317
O 2 -- Se 5	0.09	2.31973
C 2 -- O 2	0.26	2.32955
H 3 -- Pb 5	0.02	2.32990
C 2 -- Pb 6	0.64	2.39799
H 2 -- O 1	0.01	2.43038
H 1 -- O 2	0.06	2.43612
H 3 -- Pb 9	0.06	2.47909
H 2 -- Pb 5	0.14	2.51038
H 3 -- O 1	0.01	2.53472
O 2 -- Pb 5	0.05	2.56759
H 3 -- Pb 6	0.01	2.83809
H 3 -- O 2	0.02	2.86655

O 1 -- Se 5	0.13	2.87928
H 1 -- O 1	0.04	2.88228
H 2 -- O 2	0.01	2.97408

==========

All bands spilling parameter for spin component 1 = 0.99%

Hirshfeld Analysis

Species	Ion	Hirshfeld Charge (e)	Spin (hbar/2)
H	1	-0.00	0.00
H	2	-0.01	0.00
H	3	0.01	0.00
C	1	0.10	0.00
C	2	-0.21	0.00
O	1	-0.09	0.00
O	2	-0.24	0.00
Se	1	-0.34	0.00
Se	2	-0.36	0.00
Se	3	-0.35	0.00
Se	4	-0.26	0.00
Se	5	0.07	0.00
Se	6	-0.33	0.00
Se	7	-0.36	0.00
Se	8	-0.28	0.00
Se	9	-0.28	0.00
Se	10	-0.36	0.00
Se	11	-0.25	0.00
Se	12	-0.31	0.00
Se	13	-0.27	0.00
Pb	1	0.33	0.00
Pb	2	0.35	0.00
Pb	3	0.33	0.00
Pb	4	0.33	0.00
Pb	5	0.52	0.00
Pb	6	0.30	0.00
Pb	7	0.32	0.00
Pb	8	0.27	0.00
Pb	9	0.22	0.00
Pb	10	0.20	0.00
Pb	11	0.33	0.00
Pb	12	0.30	0.00
Pb	13	0.32	0.00

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Table S4| CASTEP calculation for PbSe/Cl: results I – energies

SCF loop	Energy	Fermi energy	Energy gain per atom	Timer (sec)
Initial	-7.45115027E+004	0.00000000E+000		6.15

```
    1 -6.95588890E+004  2.36418269E+000 -1.83430136E+002    179.00 ← SCF
    2 -7.21917686E+004 -2.52528588E+000  9.75140586E+001    315.89 ← SCF
    3 -7.23907130E+004 -2.31170192E+000  7.36831050E+000    431.23 ← SCF
    4 -7.23971529E+004 -2.33087421E+000  2.38515545E-001    557.17 ← SCF
    5 -7.23904933E+004 -1.78892582E+000 -2.46652443E-001    687.70 ← SCF
    6 -7.23899374E+004 -1.56303883E+000 -2.05890050E-002    838.54 ← SCF
    7 -7.23898127E+004 -1.50221275E+000 -4.61622405E-003    976.72 ← SCF
    8 -7.23897475E+004 -1.44748879E+000 -2.41711607E-003   1126.48 ← SCF
    9 -7.23897327E+004 -1.38172889E+000 -5.45386206E-004   1259.66 ← SCF
   10 -7.23897565E+004 -1.35961614E+000  8.79582632E-004   1374.81 ← SCF
   11 -7.23897709E+004 -1.33714435E+000  5.32537732E-004   1498.64 ← SCF
   12 -7.23897824E+004 -1.32309756E+000  4.28511458E-004   1605.66 ← SCF
   13 -7.23897956E+004 -1.32551746E+000  4.86941303E-004   1711.53 ← SCF
   14 -7.23897986E+004 -1.32111081E+000  1.11772950E-004   1822.59 ← SCF
   15 -7.23898009E+004 -1.32170637E+000  8.42691978E-005   1925.71 ← SCF
   16 -7.23898020E+004 -1.32199270E+000  4.20381632E-005   2026.45 ← SCF
   17 -7.23898026E+004 -1.32201299E+000  2.07389631E-005   2120.52 ← SCF
   18 -7.23898027E+004 -1.32211240E+000  5.70016094E-006   2220.03 ← SCF
   19 -7.23898028E+004 -1.32195029E+000  1.19232114E-006   2304.85 ← SCF
   20 -7.23898028E+004 -1.32177425E+000  3.11087285E-007   2386.16 ← SCF
------------------------------------------------------------------------------ ← SCF
Final energy, E            = -72389.71891100     eV
Final free energy (E-TS)   = -72389.80276092     eV
(energies not corrected for finite basis set)
NB est. 0K energy (E-0.5TS)      = -72389.76083596     eV
Writing analysis data to PbSe-Cl.castep_bin
Writing model to PbSe-Cl.check

*********************** Forces ***********************
 *          Cartesian components (eV/A)           *
 * ------------------------------------------------ *
 *              x         y         z     *
 *                                         *
 * Cl       1    -0.09134    -0.27460     0.13377 *
 * Se       1     0.03973     0.47735     0.05805 *
 * Se       2     0.00413    -0.01397     0.00513 *
 * Se       3    -0.10419    -0.03151    -0.01211 *
 * Se       4    -0.07566    -0.06699     0.00637 *
 * Se       5    -0.11088     0.24138     0.00106 *
 * Se       6     0.06653     0.08708    -0.17304 *
 * Se       7     0.04424     0.02233     0.00397 *
 * Se       8    -0.04814     0.00137    -0.05120 *
 * Se       9    -0.03240     0.04890    -0.02543 *
 * Se      10    -0.12773     0.00839    -0.00736 *
 * Se      11    -0.03490     0.00542     0.00953 *
 * Se      12    -0.05789     0.00993     0.08065 *
 * Se      13     0.00234     0.02802    -0.02340 *
 * Pb       1    -0.04918     0.02329     0.09334 *
 * Pb       2     0.07894    -0.49465     0.05325 *
 * Pb       3     0.10744     0.02842    -0.06117 *
 * Pb       4     0.00010     0.05990     0.00194 *
 * Pb       5     0.06404    -0.09084     0.04839 *
 * Pb       6    -0.00972     0.01471    -0.07717 *
```

```
 * Pb      7    0.10275     0.03491    -0.04093 *
 * Pb      8   -0.01607     0.03823     0.01125 *
 * Pb      9    0.09451    -0.19660     0.00114 *
 * Pb     10    0.00794    -0.03731     0.03160 *
 * Pb     11    0.10564     0.02478    -0.03815 *
 * Pb     12    0.02970    -0.01120    -0.02661 *
 * Pb     13    0.01006     0.06326    -0.00287 *
***************************************************
Pseudo atomic calculation performed for Cl 3s2 3p5
Converged in 19 iterations to a total energy of -405.1170 eV
Pseudo atomic calculation performed for Se 4s2 4p4
Converged in 17 iterations to a total energy of -253.2878 eV
Pseudo atomic calculation performed for Pb 5s2 5p6 5d10 6s2 6p2
Converged in 28 iterations to a total energy of -5275.7922 eV
Charge spilling parameter for spin component 1 = 0.16%
```

Table S5| CASTEP calculation for PbSe/Cl: results II – Mulliken and Hirshfeld analysis

Atomic Populations (Mulliken)

Species	Ion	s	p	d	f	Total	Charge (e)
Cl	1	1.97	5.47	0.00	0.00	7.43	-0.43
Se	1	1.99	4.50	0.00	0.00	6.48	-0.48
Se	2	2.00	4.50	0.00	0.00	6.51	-0.51
Se	3	2.00	4.54	0.00	0.00	6.54	-0.54
Se	4	1.86	4.58	0.00	0.00	6.44	-0.44
Se	5	2.01	4.48	0.00	0.00	6.50	-0.50
Se	6	1.90	4.51	0.00	0.00	6.41	-0.41
Se	7	2.01	4.54	0.00	0.00	6.55	-0.55
Se	8	1.88	4.60	0.00	0.00	6.47	-0.47
Se	9	1.89	4.55	0.00	0.00	6.45	-0.45
Se	10	2.01	4.52	0.00	0.00	6.53	-0.53
Se	11	1.84	4.58	0.00	0.00	6.42	-0.42
Se	12	1.91	4.57	0.00	0.00	6.48	-0.48
Se	13	1.86	4.58	0.00	0.00	6.43	-0.43
Pb	1	3.90	7.57	10.00	0.00	21.47	0.53
Pb	2	3.91	7.63	10.00	0.00	21.54	0.46
Pb	3	3.89	7.68	10.00	0.00	21.56	0.44
Pb	4	3.91	7.55	10.00	0.00	21.46	0.54
Pb	5	3.86	7.62	10.00	0.00	21.47	0.53
Pb	6	3.95	7.53	10.00	0.00	21.48	0.52
Pb	7	3.87	7.58	10.00	0.00	21.44	0.56
Pb	8	3.91	7.57	10.00	0.00	21.47	0.53
Pb	9	3.90	7.67	10.00	0.00	21.57	0.43
Pb	10	3.85	7.54	10.00	0.00	21.39	0.61
Pb	11	3.89	7.67	10.00	0.00	21.56	0.44
Pb	12	3.90	7.58	10.00	0.00	21.48	0.52
Pb	13	3.91	7.55	10.00	0.00	21.46	0.54

Bond	Population	Length (A)

Cl 1 -- Pb 5	0.36	2.54587
Se 3 -- Pb 3	0.33	2.61574
Se 10 -- Pb 11	0.32	2.61633
Se 5 -- Pb 9	0.33	2.65349
Se 1 -- Pb 2	0.31	2.69089
Se 6 -- Pb 5	0.34	2.73253
Se 8 -- Pb 7	0.33	2.80006
Se 2 -- Pb 4	0.08	2.80165
Se 6 -- Pb 8	0.23	2.80554
Se 2 -- Pb 1	0.04	2.80672
Se 12 -- Pb 13	0.19	2.82640
Se 12 -- Pb 3	0.06	2.85120
Se 9 -- Pb 9	0.00	2.85169
Se 8 -- Pb 1	0.21	2.85240
Se 9 -- Pb 2	0.03	2.86239
Se 13 -- Pb 12	0.06	2.87338
Se 7 -- Pb 12	0.06	2.87375
Se 12 -- Pb 11	0.07	2.87509
Se 11 -- Pb 4	0.13	2.88082
Se 11 -- Pb 12	0.28	2.88150
Se 9 -- Pb 6	0.24	2.88185
Se 2 -- Pb 8	0.07	2.90452
Se 13 -- Pb 9	0.15	2.91505
Se 11 -- Pb 13	0.05	2.91856
Se 5 -- Pb 7	0.36	2.92419
Se 13 -- Pb 7	0.07	2.93944
Se 1 -- Pb 6	0.04	2.94250
Se 7 -- Pb 7	0.29	2.94593
Se 4 -- Pb 4	0.02	2.95178
Se 4 -- Pb 1	0.01	2.95222
Se 3 -- Pb 13	0.07	2.96034
Se 6 -- Pb 6	0.30	2.96233
Se 4 -- Pb 3	0.14	2.96468
Se 4 -- Pb 2	0.14	2.97484
Se 9 -- Pb 10	0.05	2.98005
Se 13 -- Pb 11	0.18	2.98144

==========

All bands spilling parameter for spin component 1 = 0.84%

Hirshfeld Analysis

Species	Ion	Hirshfeld Charge (e)	Spin (hbar/2)
Cl	1	-0.30	0.00
Se	1	-0.27	0.00
Se	2	-0.27	0.00
Se	3	-0.30	0.00
Se	4	-0.24	0.00
Se	5	-0.24	0.00
Se	6	-0.25	0.00
Se	7	-0.27	0.00
Se	8	-0.26	0.00
Se	9	-0.25	0.00

Se	10	-0.29	0.00
Se	11	-0.23	0.00
Se	12	-0.26	0.00
Se	13	-0.24	0.00
Pb	1	0.30	0.00
Pb	2	0.29	0.00
Pb	3	0.26	0.00
Pb	4	0.31	0.00
Pb	5	0.25	0.00
Pb	6	0.28	0.00
Pb	7	0.31	0.00
Pb	8	0.28	0.00
Pb	9	0.27	0.00
Pb	10	0.23	0.00
Pb	11	0.27	0.00
Pb	12	0.29	0.00
Pb	13	0.30	0.00

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Table S6| CASTEP calculation for PbSe/I: results I – energies

SCF loop	Energy	Fermi energy	Energy gain per atom	Timer (sec)	
Initial	-7.40311175E+004	0.00000000E+000		6.19	← SCF
1	-6.89407381E+004	2.46673422E+000	-1.88532571E+002	181.21	← SCF
2	-7.16185249E+004	-1.09659765E-001	9.91772908E+001	321.61	← SCF
3	-7.18210529E+004	2.30900632E-002	7.50103530E+000	438.11	← SCF
4	-7.18273570E+004	-3.00193794E-002	2.33486158E-001	561.54	← SCF
5	-7.18152726E+004	-4.57426620E-001	-4.47569252E-001	687.84	← SCF
6	-7.18142839E+004	-6.61081462E-001	-3.66189819E-002	835.73	← SCF
7	-7.18141527E+004	-6.44485229E-001	-4.86072065E-003	972.40	← SCF
8	-7.18140418E+004	-6.51735657E-001	-4.10463392E-003	1113.36	← SCF
9	-7.18140382E+004	-6.07764989E-001	-1.34173312E-004	1246.57	← SCF
10	-7.18140436E+004	-5.72842006E-001	1.99073365E-004	1371.26	← SCF
11	-7.18140514E+004	-5.43433215E-001	2.89420992E-004	1496.63	← SCF
12	-7.18140701E+004	-5.23938608E-001	6.94004570E-004	1610.21	← SCF
13	-7.18140813E+004	-5.14257315E-001	4.13529748E-004	1724.37	← SCF
14	-7.18140880E+004	-5.10025881E-001	2.46704145E-004	1829.66	← SCF
15	-7.18140905E+004	-5.08334444E-001	9.24028130E-005	1939.19	← SCF
16	-7.18140918E+004	-5.07804379E-001	4.77464339E-005	2034.27	← SCF
17	-7.18140926E+004	-5.08015228E-001	2.96777354E-005	2130.60	← SCF
18	-7.18140927E+004	-5.08264724E-001	4.06229927E-006	2222.81	← SCF
19	-7.18140927E+004	-5.07933931E-001	1.35846223E-006	2307.79	← SCF
20	-7.18140927E+004	-5.07747522E-001	4.14448482E-007	2387.94	← SCF

Final energy, E = -71814.01844559 eV
Final free energy (E-TS) = -71814.09270950 eV
(energies not corrected for finite basis set)
NB est. 0K energy (E-0.5TS) = -71814.05557755 eV
Writing analysis data to PbSe-Cl.castep_bin

Writing model to PbSe-Cl.check

********** Forces **********
* Cartesian components (eV/A) *
 * ---------- *
 * x y z *
 * *
 * Se 1 0.32030 1.58104 0.06411 *
 * Se 2 -0.75259 0.75129 0.32064 *
 * Se 3 -1.55219 -0.24044 0.21348 *
 * Se 4 -0.31885 0.35994 -0.21850 *
 * Se 5 1.75482 1.21894 0.31654 *
 * Se 6 -0.07280 0.26796 -1.66658 *
 * Se 7 -1.01174 0.41882 0.06806 *
 * Se 8 -0.00355 -0.09522 0.26437 *
 * Se 9 -0.00466 -0.34764 0.23081 *
 * Se 10 -1.50211 -0.32179 -0.12137 *
 * Se 11 0.14093 0.24420 0.12847 *
 * Se 12 0.56279 0.12171 0.09539 *
 * Se 13 -0.28190 0.17695 0.29265 *
 * I 1 599.21207 -1698.47364 0.92822 *
 * Pb 1 0.39713 0.31758 0.58418 *
 * Pb 2 0.60064 -1.81268 0.89851 *
 * Pb 3 1.77021 -0.66410 0.84647 *
 * Pb 4 -0.29196 -0.48200 0.53298 *
 * Pb 5 -600.17084 1697.83185 0.87893 *
 * Pb 6 -0.38062 0.63088 -0.53812 *
 * Pb 7 0.20599 0.44623 -0.76648 *
 * Pb 8 0.38925 0.28818 -0.56162 *
 * Pb 9 0.48738 -1.25829 -1.07356 *
 * Pb 10 -0.18473 0.03310 -0.07344 *
 * Pb 11 1.73751 -0.62155 -0.92568 *
 * Pb 12 -0.26021 0.11338 -0.62372 *
 * Pb 13 -0.79029 -0.48472 -0.09475 *
****
Pseudo atomic calculation performed for Se 4s2 4p4
Converged in 17 iterations to a total energy of -253.2878 eV
Pseudo atomic calculation performed for I 5s2 5p5
Converged in 16 iterations to a total energy of -308.9932 eV
Pseudo atomic calculation performed for Pb 5s2 5p6 5d10 6s2 6p2
Converged in 28 iterations to a total energy of -5275.7922 eV
Charge spilling parameter for spin component 1 = 0.28%

Table S7| CASTEP calculation for PbSe/I: results II – Mulliken and Hirshfeld analysis

Atomic Populations (Mulliken)

Species	Ion	s	p	d	f	Total	Charge (e)
Se	1	1.99	4.53	0.00	0.00	6.52	-0.52
Se	2	2.00	4.57	0.00	0.00	6.56	-0.56
Se	3	2.00	4.55	0.00	0.00	6.55	-0.55

Se	4	1.86	4.58	0.00	0.00	6.44	-0.44
Se	5	1.88	4.75	0.00	0.00	6.63	-0.63
Se	6	1.86	4.77	0.00	0.00	6.63	-0.63
Se	7	1.87	4.68	0.00	0.00	6.56	-0.56
Se	8	1.89	4.60	0.00	0.00	6.50	-0.50
Se	9	1.92	4.57	0.00	0.00	6.49	-0.49
Se	10	2.01	4.56	0.00	0.00	6.57	-0.57
Se	11	1.87	4.57	0.00	0.00	6.43	-0.43
Se	12	1.92	4.58	0.00	0.00	6.51	-0.51
Se	13	1.88	4.58	0.00	0.00	6.46	-0.46
I	1	1.97	4.16	0.00	0.00	6.12	0.88
Pb	1	3.94	7.54	10.00	0.00	21.48	0.52
Pb	2	3.95	7.61	10.00	0.00	21.56	0.44
Pb	3	3.94	7.61	10.00	0.00	21.55	0.45
Pb	4	3.95	7.53	10.00	0.00	21.48	0.52
Pb	5	3.37	8.47	10.02	0.00	21.86	0.14
Pb	6	3.98	7.60	10.00	0.00	21.57	0.43
Pb	7	3.95	7.53	10.00	0.00	21.47	0.53
Pb	8	3.96	7.56	10.00	0.00	21.52	0.48
Pb	9	3.94	7.64	10.00	0.00	21.57	0.43
Pb	10	3.90	7.54	10.00	0.00	21.44	0.56
Pb	11	3.94	7.61	10.00	0.00	21.55	0.45
Pb	12	3.94	7.56	10.00	0.00	21.49	0.51
Pb	13	3.95	7.53	10.00	0.00	21.47	0.53

Bond	Population	Length (A)
I 1 -- Pb 5	0.28	0.95000
Se 6 -- Pb 5	1.63	2.80869
Se 6 -- I 1	0.63	2.91452
Se 5 -- I 1	1.56	2.91822
Se 7 -- Pb 5	2.54	2.99511
Se 3 -- Pb 3	0.33	2.61574
Se 10 -- Pb 11	0.32	2.61633
Se 5 -- Pb 9	0.33	2.65349
Se 1 -- Pb 2	0.31	2.69089
Se 6 -- Pb 5	0.34	2.73253
Se 8 -- Pb 7	0.33	2.80006
Se 2 -- Pb 4	0.08	2.80165
Se 6 -- Pb 8	0.23	2.80554
Se 2 -- Pb 1	0.04	2.80672
Se 12 -- Pb 13	0.19	2.82640
Se 12 -- Pb 3	0.06	2.85120
Se 9 -- Pb 9	0.00	2.85169
Se 8 -- Pb 1	0.21	2.85240
Se 9 -- Pb 2	0.03	2.86239
Se 13 -- Pb 12	0.06	2.87338
Se 7 -- Pb 12	0.06	2.87375
Se 12 -- Pb 11	0.07	2.87509
Se 11 -- Pb 4	0.13	2.88082
Se 11 -- Pb 12	0.28	2.88150
Se 9 -- Pb 6	0.24	2.88185
Se 2 -- Pb 8	0.07	2.90452

Se 13 -- Pb 9	0.15	2.91505
Se 11 -- Pb 13	0.05	2.91856
Se 5 -- Pb 7	0.36	2.92419
Se 13 -- Pb 7	0.07	2.93944
Se 1 -- Pb 6	0.04	2.94250
Se 7 -- Pb 7	0.29	2.94593
Se 4 -- Pb 4	0.02	2.95178
Se 4 -- Pb 1	0.01	2.95222
Se 3 -- Pb 13	0.07	2.96034
Se 6 -- Pb 6	0.30	2.96233
Se 4 -- Pb 3	0.14	2.96468
Se 4 -- Pb 2	0.14	2.97484
Se 9 -- Pb 10	0.05	2.98005
Se 13 -- Pb 11	0.18	2.98144

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All bands spilling parameter for spin component 1 = 0.87%

Hirshfeld Analysis

Species	Ion	Hirshfeld Charge (e)	Spin (hbar/2)
Se	1	-0.34	0.00
Se	2	-0.36	0.00
Se	3	-0.35	0.00
Se	4	-0.27	0.00
Se	5	-0.35	0.00
Se	6	-0.37	0.00
Se	7	-0.37	0.00
Se	8	-0.28	0.00
Se	9	-0.30	0.00
Se	10	-0.36	0.00
Se	11	-0.25	0.00
Se	12	-0.31	0.00
Se	13	-0.26	0.00
I	1	0.28	0.00
Pb	1	0.32	0.00
Pb	2	0.34	0.00
Pb	3	0.34	0.00
Pb	4	0.33	0.00
Pb	5	0.26	0.00
Pb	6	0.24	0.00
Pb	7	0.34	0.00
Pb	8	0.26	0.00
Pb	9	0.32	0.00
Pb	10	0.20	0.00
Pb	11	0.34	0.00
Pb	12	0.30	0.00
Pb	13	0.32	0.00

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